

A High Pressure Carbon Dioxide Separation Process for IGCC Plants

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1.0 INTRODUCTION

Under separate contracts from the U.S. Department of Energy, Office of Fossil Energy (DOE-FE), Los Alamos National Laboratory, and a team of SIMTECHE and Nexant (a Bechtel Technology and Consulting Company) are jointly working to develop the proprietary process for capturing carbon dioxide (CO₂) from a shifted syngas stream (a mixture of mostly carbon dioxide and hydrogen) prior to combustion in an IGCC plant. This innovative approach, using the proprietary SIMTECHE Process, separates CO₂ from the shifted syngas with water at lower temperature than those in the existing absorption and adsorption approaches. The initial phase (18 months) of this four-phase, sixty six-month program consists of analytical and theoretical research and development studies as well as engineering analysis, both to further assess the efficiency and economic benefits of the SIMTECHE process and to better understand the micro- and macro-scale physics of the processes involved. The second phase (21 months) will consist of further laboratory-scale tests, which will be performed in parallel with the design and fabrication of a skid-mounted pilot plant. The third phase (15 months) will consist of laboratory-scale and pilot plant tests to further establish the proof-of-concept and to provide detailed design and operating data in preparation for pilot plant field tests. In the final phase (12 months), the pilot plant will be decommissioned and relocated to an existing IGCC power plant for final process evaluation with the shifted syngas from an industrial operating gasifier.

In this paper, the issue of carbon dioxide separation from shifted synthesis gas at elevated pressures is addressed. Focus is placed on the low temperature, high pressure SIMTECHE process. This process is based on formation of gas hydrates rich in carbon dioxide. The equilibrium thermodynamic limits of such a process are discussed and the results of equilibrium hydrate formation experiments are presented for selected shifted synthesis gas compositions. The enhancement of carbon dioxide hydrate formation and separation in the presence of gaseous and/or liquid promoters is also discussed. A bench-scale flow system for the continuous production of carbon dioxide hydrates is then described and operational issues associated with continuous hydrate production are identified. Finally, plans for continued development of the process are outlined.

Updated results on process evaluations of SIMTECHE's CO₂ hydrate separation process are presented. Performance projections are made using newly obtained experimental data. The results of several prior process evaluations indicated that the process is competitive with the existing commercial CO₂ separation processes, such as amine absorption. However, these prior studies were based on limited experimental data from the California Institute of Technology. The process configuration was revised to incorporate the lessons learned from the current R&D program. This paper summarizes the results of this latest process evaluation. The conceptual design of the SIMTECHE process, and its integration into an advanced IGCC plant, is presented. The previous capital and operating costs are updated for estimating the CO₂ capture cost in dollars per ton of carbon avoided. The future plan to design, fabricate, and operate a larger pilot plant is also discussed.

2.0 OBJECTIVES

The primary overall objective of the Phase 1 program is to analytically and experimentally confirm the feasibility of the proposed SIMTECHE Process, i.e. demonstrate the "Proof of Concept" performance. Other objectives in Phase 1 are to:

- (1) Extend the previously developed process modeling to the latest proposed concept for the SIMTECHE Process,
- (2) Assess the impacts of the experimental findings on the overall process economics and identify critical properties and critical parameters, and
- (3) Determine ultimate reduction in carbon dioxide concentration that can be achieved and assess the potential influence of H₂S and other CO₂ hydrate promoters and elevated pressures on the process.

3.0 EXPERIMENTAL PROGRAM

The Phase 1 experimental program consists of "proof-of-concept" experiments and collection of data useful in the engineering analysis and design of the pilot plant in Phase 2. However, the main focus is in the "proof-of-concept". The main areas of investigation are:

- Equilibrium pressure/temperature of hydrate formation, and the effect of so-called "promoters". This will enable the prediction of CO₂ removal performance of the process in the range of process conditions expected.
- Composition of the hydrate and the heat of formation of the mixed hydrates of interest. This will enable the prediction of the heat removal requirements of the hydrate formation reactors and the composition of the CO₂ gas stream to be sequestered.
- Performance of small-scale reactors in continuous-flow formation of hydrates. The main areas of interest are in the performance of the bench-scale reactors (versus ideal performance), in the cooling performance (heat transfer coefficients), and in assuring effective phase contacting (proper multiphase flow regime).

The approach used in the experimental program is to build on past work in characterizing CO₂ hydrates, small-scale continuous-flow experiments and engineering analysis. Equilibrium data was collected using a Parr Instruments high-pressure batch autoclave reactor, with conditions closer to the range of conditions expected in the SIMTECHE process. After confirming the

performance of the apparatus with pure CO₂ and water, experimental conditions have been focused on expected syngas compositions and pressures, and in the presence of proprietary hydrate promoters. The approach to the flow experiments has been to validate the performance of the system in repeating previous results, and then to develop continuous flow experiments with larger reactors and more complete measurement systems. The larger reactors are configured to yield data for design of a scaled-up system.

3.1 EQUILIBRIUM EXPERIMENTAL RESULTS

Results from CO₂/H₂S/H₂ experiments indicate that little, if any, hydrogen is involved in hydrate formation. Thus hydrogen behaves essentially as an inert and is not incorporated into the hydrate crystal. Batch equilibrium data experiments were then conducted with various binary gas mixtures as shown in Table 3-1. These experiments were planned to investigate the impacts of gas compositions and concentrations on the hydrate formation temperature and pressure.

Table 3-1 Composition (mole %) of Gas Mixtures in the Equilibrium Experiments

Gas Mixtures	H ₂	H ₂ S	CO ₂
A	60	0	40
B	0	3	97
C	0	5	95
D	0	1	99

One set of the results from gas mixture B is plotted in Figure 3-1. As shown, when the system is cooled from room temperature, the pressure drops linearly until clathrates begin to form. Then, a sharp spike in temperature is observed indicating initial clathrate formation. The system is cooled below this temperature and then slowly reheated to insure that the system is in equilibrium. The point at which the cooling curve and the heating curve become parallel is taken as the equilibrium pressure and temperature. These data show that the addition of 3 mole % H₂S significantly increases the clathrate equilibrium temperature or alternatively, reduces the equilibrium pressure compared to the phase line for pure CO₂. Figure 3-2 summarizes the results from the equilibrium experiments with the different gas mixtures.

At the time of preparing this paper, additional equilibrium experiments are underway to obtain data to determine the hydrate composition and effects of other hydrate promoters. Some of these additional results will be presented in the NETL Carbon Sequestration Conference. The current equilibrium data have confirmed the projected performance of CO₂ separation ratio in an impure shifted synthesis gas containing 1.1% H₂S by volume. The theoretical projections of minimum CO₂ hydrate formation pressures for various H₂S concentrations are generally within 10% of the experimental data.

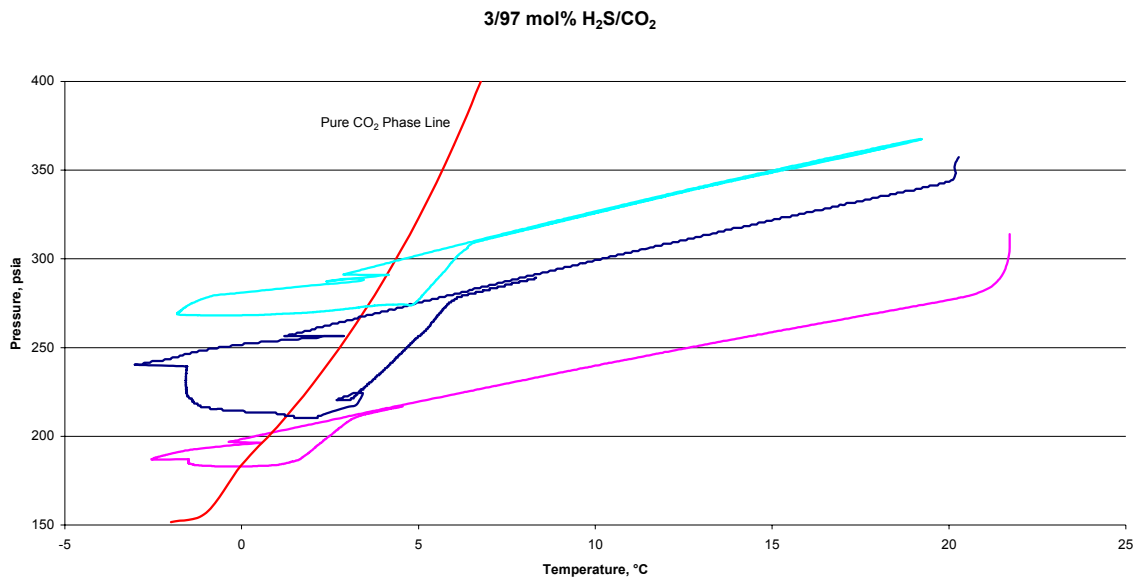


Figure 3-1 Equilibrium Experimental Data with a 3/97 mol% H₂S/CO₂ Mixture

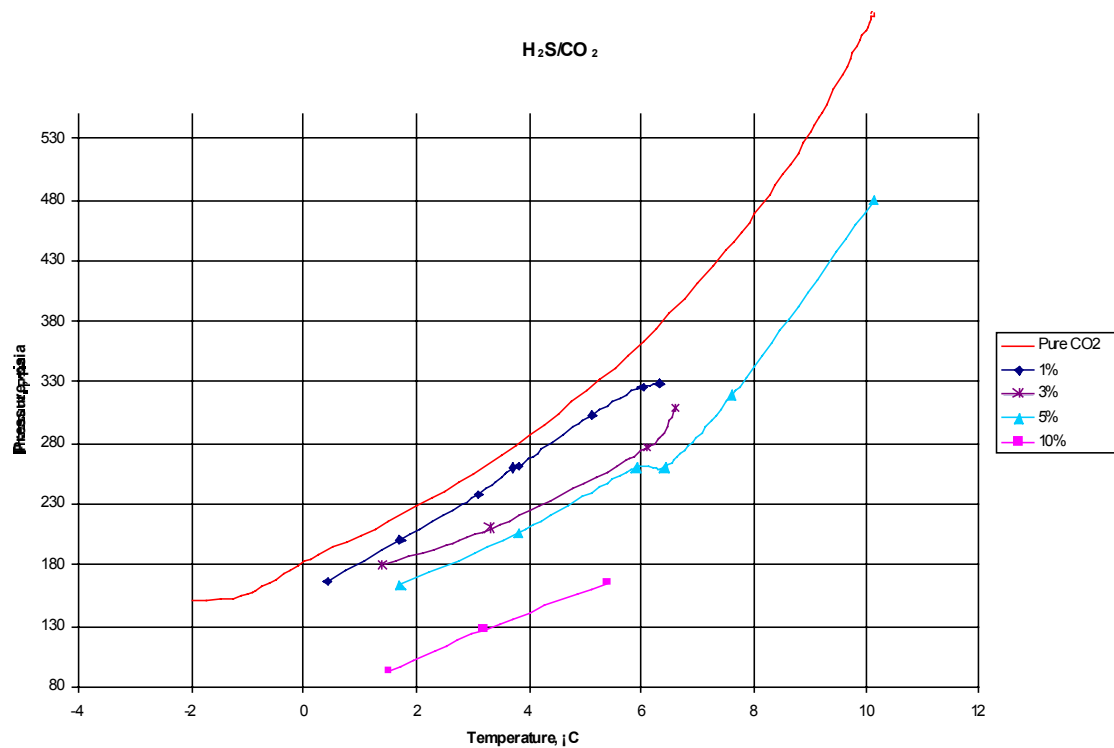


Figure 3-2 Measured hydrate formation pressure as a function of temperature for various H₂S percentages.

3.2 H₂S AS A HYDRATE PROMOTER

As shown in Figure 3-2, the equilibrium data also illustrate that the absolute partial pressure of H₂S is an important controlling variable that can be exploited. With constant mole fractions of H₂S and CO₂ in a shifted synthesis gas stream, the partial pressure of H₂S increases with increasing total system pressure; thus the minimum hydrate formation pressure decreases. Quantitatively, the final equilibrium point will depend on both the H₂S and CO₂ partial pressures. Generally, an increased system pressure should result in a greater separation of the hydrate formers from the gas stream as a result of both 1) the increased partial pressure of CO₂ and 2) a beneficial effect from a simultaneous increase in H₂S partial pressure that lowers the equilibrium hydrate formation pressure further. Measurements are underway to determine the composition of the resulting hydrates as a function of CO₂/H₂S partial pressures.

3.3 CONTINUOUS FLOW HYDRATE REACTOR

A bench-top continuous flow apparatus has been set up and tested. This unit involves CO₂ flows on the order of one gram-mole/min (in excess water) and has been run for continuously for periods of many minutes (as opposed to seconds, as was done in the earlier experimental program). With proper control of phase contacting, a significant amount of hydrate can be formed in the flow system. Specifically, with proper mixing, the kinetics of hydrate formation appears to be quite favorable. In fact, plugging of the small-scale system with hydrate has been observed. Preliminary energy balances suggest that conversions as high as 35% to hydrate can be obtained and separate analysis indicates that global performance of the unit may be heat transfer-limited with the current design. Detailed heat and material balance data will not be presented until the unit is fully commissioned. Operationally, key issues appear to be phase contacting and preservation of favorable multiphase flow regimes, effective heat transfer for removal of the heats of solution and formation, and operating strategies which avoid formation of hydrate plugs. We are currently assessing the impact scale-up to larger diameter equipment will have on these operational issues.

4.0 ENGINEERING ANALYSIS

In a separate 1999 DOE study, Nexant evaluated the feasibility of the SIMTECHE Process in an IGCC plant with different advanced power plant configurations. The current study revises the base case SIMTECHE design in the 1999 Study in light of new experimental data and lessons learned in order to assess their impacts on the overall process economics, to identify critical properties and critical parameters, to develop the sensitivity of the cost of sequestration to variances in design parameters and do a comparison with conventional CO₂ removal systems.

Conceptual designs of the IGCC plant with and without CO₂ capture are developed, and then capital and operating costs are estimated which enable a cost of sequestration to be quantified. Important design parameters are varied and the impact upon the cost is estimated. These efforts provide an indication of the areas in which accurate laboratory data is most crucial, and areas for which design optimization will be the most beneficial. Table 4-1 lists the parameters and their ranges investigated in the sensitivity study.

Table 4-1
Design Parameters for Cost Sensitivity Study

Design Parameters	Base Case	Variation
Reactor Feed Pressure, psia	1,000	-200
Hydrate Heat of Formation, Btu/lb hydrate	490	343 - 520
Reactor Efficiency	95	85 - 100
Slurry Concentration, wt% hydrate	61	40
Hydrate Flash reactor Temperature, °F	54	43

In this paper, the base case IGCC plant configuration and the preliminary results of the current engineering analysis are discussed.

4.1 IGCC PLANT CONFIGURATION

The conceptual design of the IGCC plant includes the following major process steps:

- A. a high pressure Texaco gasifier, with the required feed handling and preparation facilities, to generate the syngas,
- B. a radiant cooler followed with water quench of the syngas to maximize sensible heat recovery from the gasifier,
- C. an air separation unit to produce 95% purity oxygen required for gasification,
- D. a two stage catalytic shift reactor to produce a predominantly H₂- CO₂ rich gas,
- E. the SIMTECHE CO₂ hydrate separation process to remove the CO₂ ,
- F. additional product gas cleaning, i.e. H₂S removal and sulfur recovery, and
- G. power generation using an advanced syngas-fueled gas turbine power cycle.

Figure 4-1 shows the overall block flow diagram of the SIMTECHE Process. While the overall SIMTECHE plant configuration is similar both in the 1999 and present engineering analysis, performance and operating conditions for the latest analysis are consistent with the LANL experimental data.

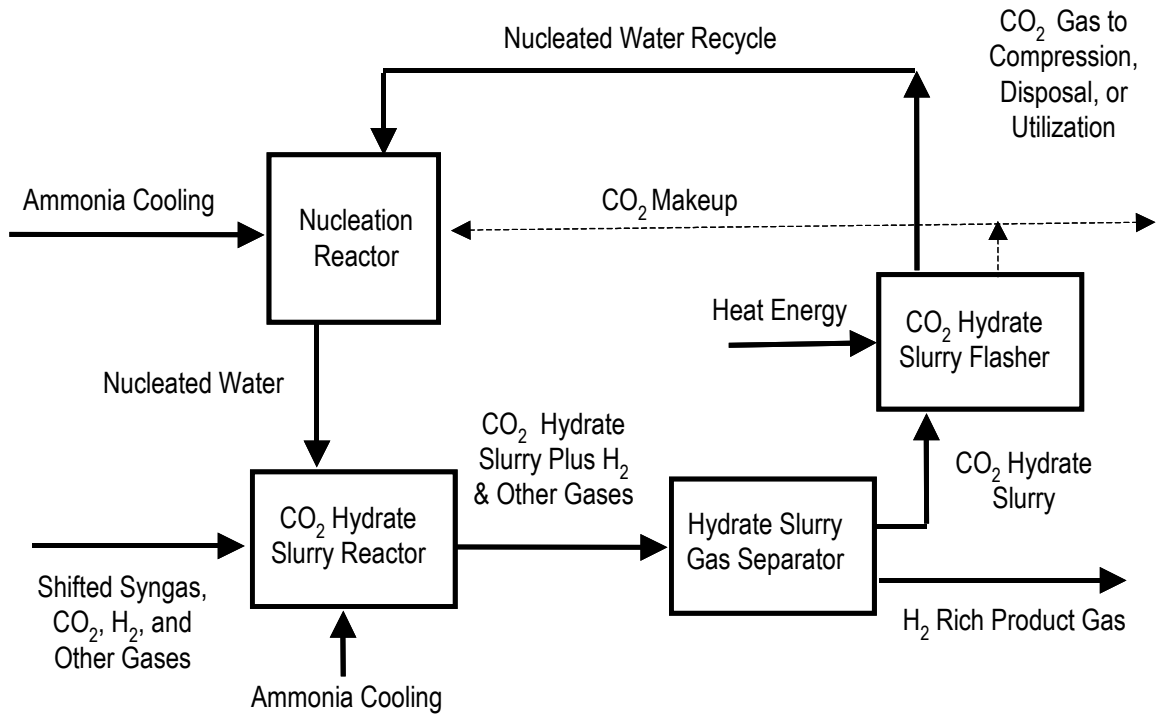


Figure 4-1 CO₂ Hydrate Process For Gas Separation From A Shifted Synthesis Gas Stream (High Pressure CO₂ Regeneration for Disposal or Utilization)

4.2 RESULTS OF THE ENGINEERING ANALYSIS

The following are the results from the engineering analysis. Table 4-2 shows the estimated capital cost for each case. The Base Case is an IGCC plant with shifted syngas feed and without any CO₂ capture. Case 1 is an IGCC plant with CO₂ capture using the SIMTECHE process. Case 2 is an IGCC plant with CO₂ capture using an MDEA amine system removing the same amount of CO₂ as the SIMTECHE process. Case 3 is an IGCC plant with CO₂ capture using a Selexol system, removing 90% of the CO₂.

Table 4-3 shows the cost of carbon control in reference to an Advanced GT-based IGCC without CO₂ control. The capital charge is assumed at 18% per year. The coal cost is assumed to be \$1.05/MM Btu (HHV). The base case is used to estimate the cost of electricity, and this cost is used to calculate the operating deficit compared to the base case. The operating deficit is divided by the tons of CO₂ removed to obtain the cost of carbon control. These are in-plant costs for carbon control, and do not include pipelining and sequestration costs.

Table 4-2
Estimated Capital Cost Comparison, 2001 US\$

	Basis: US Gulf Coast			
Case	Base	SIMTECHE	Amine	Selexol
Coal Feed, Short Tons/Day	5,000	5,000	5,000	5,000
Carbon Dioxide Captured, Short Tons/Year	0	2,417,000	2,417,000	2,417,000
Percentage Removal	0	64	64	64
Capital Cost, \$millions, 2Q-2001				
Gasifier/ASU	257.6	257.6	257.6	257.6
CO2 Removal		47.2	79.2	104.7
GT/Sulfur/BOP	361.0	327.3	327.3	324.4
Project Contingency	154.7	165.1	166.0	171.7
Total Capital Cost \$millions	773.3	797.2	830.1	858.4
Added Capital Cost \$millions	Base	23.9	56.9	85.1

Table 4-3
Estimated Cost Of Carbon Control, 2001 US\$
(Reference to the Base Case IGCC Plant)

Case	Basis: 2001 US Dollars			
	Base	SIMTECHE	Amine	Selexol
Coal Feed, Short Tons/Day	5,000	5,000	5,000	5,000
Carbon Dioxide Captured, Short Tons/Year	0	2,417,000	2,417,000	2,417,000
Percentage Removal	0	64	64	64
Cost of Production, \$Millions/yr	196.4	201.6	207.7	213.4
Power Generated, Mwe	534.8	528.3	468.2	520.1
Power Losses, Mwe	0	32.8	38.5	31.8
Net Power Plant Efficiency, %HHV	40.4	37.5	32.5	36.9
Parasitic Power Loss, %		7	20	9
Power Generation Cost, \$/Mw-hr	41.91	46.45	55.18	49.88
Yearly Revenue Loss, \$millions	Base	\$19.69	\$49.96	\$34.10
Cost of Carbon Control, \$/Short Ton CO ₂	Base	\$8	\$21	\$14

Table 4-4 shows the results of the sensitivity cases.

Table 4-4
Effect of Design Parameters on Cost of Carbon Control

Parameter	Case	Value	Effect on Cost of Carbon Control
Heat of Formation, BTU/lb Hydrate	Base	442	Base
	High	520	+6%
	Low	343	-9%
Reactor Pressure, Psia	Base	1000	Base
		900	-1%
		800	-2%
Reactor Efficiency	Base	95%	
	High	100%	
	Low	85%	
Hydrate Weight % in slurry	Base	61%	Base
		40%	+8%
Low Flash Temperature, °F	Base	54	Base
	Low	42	-8%

5.0 CONCLUSIONS

The preliminary results of the experimental program confirm the results and observations from the earlier experiments performed in California Institute of Technology. Results from the updated engineering analysis and the sensitivity study indicate that incorporation of the recently obtained experimental data into the conceptual plant design do not change the previous conclusion that SIMTECHE process holds promise as a superior method of carbon dioxide separation and delivery of high-pressure gas for sequestration in IGCC electric power generation. Parasitic power losses can be less than conventional carbon capture methods, and the capital cost may also be considerably lower. More quantitative comparisons will be presented as additional experimental data become available and are subsequently incorporated into the engineering analysis.

6.0 FUTURE ACTIVITIES

Phase 1 has been completed, with results that warrant further development in phase 2. Key areas of development for a successful pilot plant include:

- Hydrate reactor design. The hydrate formation reactors require adequate residence time and gas/liquid mixing for hydrate formation, and large heat removal duty.
- CO₂ Regenerator design. Regeneration of the CO₂ requires accurate regulation of heat input to recover the CO₂ and retain residual nucleation sites (also referred to as subcritical nuclei) in the recycled water.
- Continuous measurement systems for process diagnostics. Evaluation of the performance of the system must be adequately measured to enable a thorough evaluation of the process, as well as for troubleshooting and optimization. Due to the large refrigeration requirement, the performance of the process will depend heavily on accurate measurement of the hydrate characteristics and the characteristics of the recycled nucleated water.

The SIMTECHE pilot plant is being designed as a modular unit, to be initially operated during Phase 3. Upon successful demonstration of the system, phase 4 will be implemented. This will include relocation of the pilot plant to a gasification facility for operation in an industrial environment.